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(54) **Process for the removal of caffeine from green coffee and process for the recovery of caffeine.**

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(73) Proprietor: **SOCIETE DES PRODUITS NESTLE S.A., Case postale 353, CH- 1800 Vevey (CH)**

(72) Inventor: **Green, David, Rue de la Cité 14, CH- 1373 Chavornay (CH)**
Inventor: **Blanc, Maurice, Résidence de la Côte 30, CH- 1110 Morges (CH)**

(74) Representative: **Andrae, Steffen, Dr., Patentanwälte Andrae, Flach, Haug, Kneissl Steinstrasse 44, D-8000 München 80 (DE)**

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Description

Process for the removal of caffeine from green coffee and process for the recovery of caffeine

This invention is concerned with the recovery of caffeine from aqueous media.

In the preparation of decaffeinated coffee, two basic approaches are available for the extraction of caffeine from the beans. According to the first, green (un-roasted) coffee beans are extracted with water or an aqueous solution containing non-caffeine green coffee solids, the aqueous extract is separated from beans, caffeine is removed from the extract, usually by solvent extraction or adsorption on a solid adsorbent such as activated charcoal (see EP-A-0 008 398 and FR-A-779 451) and the caffeine-free extract may be returned to the coffee beans. The second approach involves direct contact between the beans and the caffeine solvent, usually methylene chloride, and evaporation of the solvent leaving behind the caffeine, of the various solid adsorbents that have been proposed, activated carbon offers certain advantages over substances such as polymeric resins because of its ready availability and ease of regeneration. However, it has been observed that contact between the aqueous extract and active carbon frequently leads to an increase of pH which is associated with a deterioration in the colour and favour of the coffee beans.

It has now been found that the undesirable increase of pH may be considerably diminished if the activated carbon used shows a substantially neutral reaction on dispersion in water.

The invention thus provides a process for the recovery of caffeine from an aqueous solution of caffeine extracted from green coffee beans and non-caffeine green coffee solids which comprises contacting the solution with activated carbon and separating the activated carbon, with caffeine adsorbed thereon, from aqueous solution of reduced caffeine content, characterised in that the activated carbon used is a neutralised carbon that when it is immersed in distilled water the pH value of the water is substantially unchanged. Carbon having this property may be obtained either by acid washing of thermally activated carbon followed by rinsing with water to neutrality, or by neutralisation of acid-activated carbon with an aqueous alkali followed by rinsing with water to neutrality. Preferably, the caffeine content of the aqueous solution is reduced substantially to zero.

According to another aspect of the invention there is provided a process for the removal of caffene from green coffee beans which comprises contacting the beans with an aqueous medium selected from the group consisting of water, an aqueous solution of non-caffeine green coffee solids and an aqueous solution of non-caffeine green coffee solids containing a minor amount of caffeine, recovering aqueous medium containing caffeine dissolved from the green coffee beans, removing caffeine from the medium, recovering aqueous medium of reduced caffeine content and combining non-caffeine green coffee solids in the aqueous medium of reduced caffeine content with green coffee beans having a reduced content of caffeine and of non-caffeine green coffee solids characterised in that the caffeine is removed by the process for recovering caffeine defined in the preceding paragraph.

The aqueous caffeine solution is obtained by conventional methods, involving contact of green coffee beans with water for a period time sufficient to reduce the caffeine content of the beans to the desired level. The contacting may be effected in a counter-current system, using an arrangement similar to those used for extracting roasted coffee in the preparation of coffee extract, or batch contact may be employed wherein a fixed volume of water is continuously recycled to a fixed weight of coffee beans, caffeine being removed from the extract at each cycle prior to is being returned to the beans. In the counter-current system, the aqueous extraction medium containing caffeine and non-caffeine green coffee solids encounters coffee of progressively higher caffeine content. On leaving the system, the caffeine-laden extract is contacted with the adsorbent, preferably again in a counter-current column system. The main factors affecting the operation are temperature, the ratio of extraction liquid to coffee, the ratio of carbon to coffee, time and liquid velocity, each of which may be adapted to the degree of decaffeination desired, which is preferably such that the caffeine content is reduced substantially to zero. In carrying out the process according to the invention the neutral activated carbon may be used either in the batch or the counter-current continuous system. In both cases provision is usually made for continuity of operation by duplicating the beds of adsorbent so that one or more may be renewed whilst the others are on stream.

Decaffeination of green coffee beans is preferably effected with deionised water; the water to coffee ratio is by no means critical, but rather is determined having regard to practical considerations imposed by industrial operations. Excessive volumes are thus avoided, as also water to coffee ratios which do not provide for adequate caffeine extraction. It has been found that in general a weight ratio of water to green coffee of at least about 3 parts of water per part of coffee gives satisfactory results.

In one preferred, embodiment, green coffee beans are contacted as a static bed, in a column, or in a suitable tumbler or like extractor. In both cases, the weights of coffee and water are constant, with the caffeine-laden water withdrawn from the column or extractor being decaffeinated with neutral activated carbon prior to its being recycled. The weight of carbon is usually 20 to 30 % of the weight of green coffee being decaffeinated. The total contact time will depend, inter alia, on the water/coffee ratio, temperature and the degree of decaffeination desired. In most cases it is 3 to 10 hours. The temperature is preferably in the range 60 to 90° C. Lower temperatures are usually avoided as the risk of microbial growth, especially with long contact times, is increased, resulting in fermentation of the sugars present in the extrac. In addition, the rate of caffeine diffusion from the beans decreases with temperature. Above 90° C, with long contact times, flavour may be

impaired and as a practical matter it is difficult to maintain these temperatures without resort to pressurised equipment.

In another preferred embodiment of the invention, applied to continuous extraction and decaffeination of green coffee beans, a counter-current system is used.

The green coffee is extracted using an arrangement similar to those used for extracting roasted coffee. The fresh water entering the most exhausted extractor is normally at a temperature in the range 90 to 120°C. Deionised water is used for preference. The water to coffee ratio is not critical but is generally between 3 : 1 and 15 : 1 by weight. The number of extractors and cycle time are chosen to give the desired degree of decaffeination. Up to eight extractors, in series, may be used with a cycle time of between 15 and 120 min.

The aqueous extract (solution or medium) containing caffeine and non-caffeine green coffee solids preferably has a solids content not exceeding 10 % by weight and it may be concentrated up to this limit before being decaffeinated by contacting with neutralised, activated carbon, for example in a counter-current system. In this system the carbon is contained in several columns and the extract passes through these columns in series. Periodically the most saturated column is removed from the system and one containing fresh carbon added. The temperature in the columns is preferably between 60 and 90°C. The number of columns, the cycle time for each column and the residence time of the extract are chosen to achieve the degree of decaffeination desired and to minimise the quantity of carbon used. The weight of carbon is usually 10 - 20 % of the weight of green coffee being decaffeinated.

In the batch/recirculation system, contact temperature between carbon and extract should desirably be at least about 60°C to avoid microbiological problems, whereas in a column arrangement the inlet temperature should be a little higher for the same reason. No well-defined relationship between temperature and caffeine adsorption has been observed.

Since the activated carbon adsorbs acids as well as caffeine, the pH of the aqeuous extract rises, reaching a maximum of 6.0 to 7.5. However, as the operation proceeds, the pH falls again so that when, for example, 97 % decaffeination is attained, it has risen by less than 1 unit over the natural pH of an aqueous green bean extract. In contrast, the pH of a green bean extract contacted with non-neutralised activated carbon rises to above 9.0, which possibly explains the deterioration in colour and favour.

By way of illustration, the results obtained when different activated carbons are employed in the batchwise manner described above are given below. A deionised water/coffee ratio of 4 : 1 by weight is used, 24 % carbon based on the weight of green coffee and the temperature of the system maintained at 70°C during 8 hours.

Carbon	pH of carbon in distilled water at 20°C	Max. pH of extract at 20°C	Final pH of extract at 20°C
A. Thermallyactivated, non-neutralised			
A1	10,8	9.4	7.2
A2	11.2	9.6	7.0
A3	9.5	9.5	7.1
B. Thermally activated, neutralised			
B1	7.5	6.7	6.2
B2	7.7	6.2	5.9
B3	7.4	6.5	5.5
C. Acid activated neutralised			
C1	6.2	6.5	6.4

When decaffeination is terminated, it is usually desirable, to avoid excessive losses, to return he non-caffeine solids present in the aqueus extract to the decaffeinated green beans. Various techniques may be used. For example, the beans may be pre-dried, usually to 10 - 45 % by weight moisture and combined directly with the extract. Alternatively the extract may be pre-concentrated, e.g. by evaporation to a solids content of 15 - 55 % by weight before contact with the beans. Satisfactory reincorporation of the solids is obtained in 4 to 8 hours, preferably at 60 - 80°C. Desirably, the total amount of water present is such that the final moisture content of the beans does not exceed about 55 % by weight. The "total" water is made up of the residual moisture of the pre-dried beans and the water present in the aqueous extract. After reincorporation of solids the coffee is dried to a moisture content of 5 - 12 % by weight before being roasted. In a modification, the amount of non-caffeine solids contacted with the coffee beans may be less than the amount extracted during decaffeination.

Periodically the active carbon may be regenerated, usually by heating or solvent extraction.

The invention is illustrated by the following Examples, in which all parts, ratios and percentages are expressed on a weight basis unless otherwise stated.

Example 1

Neutralized activated carbon is prepared by washing commercial thermally activated carbon with 2 % hydrochloric acid followed by rinsing with deionised water (pH = 6.0) until the pH of the washings is constant at 6.0. 2000 parts of green coffee beans are loaded into a tumbler extractor together with 7000 parts of deionised water. The temperature is raised to (and maintained at) 80°C. Solution is withdrawn from the extractor and recirculated at a rate of 15000 parts/hour, passing through a column containing 230 parts of the neutralised activated carbon, before returning to the extractor. After one hour, a second column also containing 230 parts of neutralised activated carbon is connected in series with the first.

After 5 hours total operation, recirculation is stopped and the extract, having a pH of 6.2, is separated from the beans. The beans are dried to 20 % moisture and mixed with the extract, which has first been concentrated to 20 % solids. Mixing is continued for 6 hours at 65°C. Thereafter, the coffee, containing 45 % moisture, is dried to a 8.5 % moisture content.

The coffee is 97 % decaffeinated and has a good appearance, similar to the original, non-decaffeinated beans but somewhat danger in colour. When roasted and prepared as an infusion, the brew is described by a panel of trained tasters as being of good quality and colour. When milk is added to the cup, the brew assumes a red-brown colour, without traces of greyness.

Examples 2 to 4

The coffee decaffeination procedure described in Example 1 is repeated with various modifications in materials and operating parameters. The results are summarised in Table I.

Table I

Ex.	pH of* carbon	Water/coffee ratio	Carbon as % of coffee	Temp °C	Total time hours	Extract final pH	% Decaff. of coffee
1	7.5	3.5	23	80	5	6.2	97
2	7.5	3.5	23	65	7	6.2	97
3	7.5	3.5	23	80	5	6.0	97
4	7.4	4.0	25	65	8	5.5	97

*measured in distilled water at 20° C.

After decaffeination, the non-caffeine solids are combined with the decaffeinated beans.

Example 5

Green coffee beans are decaffeinated continuously by counter-current extraction with an aqueous solution. 6 extractors in series are used, each containing 60 kg of green coffee. Extraction is carried out with deionised water at 100°C entering the most exhausted extractor. An aqueous solution containing caffeine and non-caffeine green bean solids is removed at 80°C from the extractor containing the least exhausted coffee. The last extractor containing decaffeinated coffee is removed from the system and one containing fresh green coffee beans added once per hour. The ratio of water to green coffee beans is 10 : 1 so that the flow rate of water entering the system is 600 lt/hr.

The extract coming from the least exhausted green coffee is passed counter-currently through 3 columns in series, each column containing 35 kg of neutralised, activated carbon prepared in a manner similar to that described in Example 1. The temperature in the columns s maintained at 75°C. The most saturated carbon column is removed and a fresh one added every four hours.

The decaffeinated green beans are dried to 20 % moisture and mixed with the corresponding quantity of decaffeinated extract, which has first been concentrated to 20 % solids. Mixing is continued for 6 hours at 75°C. Thereafter, the coffee containing 45 % moisture is dried to 9.0 % moisture content.

Table II summarises the results of tasting by a trained panel of beverages obtained from coffee decaffeinated in accordance with Examples 1, 2 and 5 and roasted. These coffees are compared to coffees decaffeinated in a manner similar to that described in Example 1, but using the carbon employed in Example 1 which has not been acid neutralised and which gives a pH of 10.8 in distilled water (A) and a carbon which gives a pH of 9.5 in distilled water (B).

Table II

Ex.	pH of* carbon	Aroma	Taste	Colour + milk	Rank	Hedonic scale
1	7.5	Good, fresh	Good, full clean, balanced	Red brown	3	6.9
2	7.5	Good, full	Good, acid clean, flavoury	Red brown	1	7.1
5	7.5	Fresh, aromatic	Natural, clean, mild, balanced	Red brown	1	7.1
A	10.8	Weak	Sl. nutty, harsh, acid, papery	Grey brown	4	4.2
B	9.5	Sl. nutty, Sl. bready	Aggressive, sl. nutty, old	Greyish brown	5	4.1

*measured in distilled water at 20°C.

Claims

1. A process for the recovery of caffeine from an aqueous solution of caffeine extracted from green coffee beans and non-caffeine green coffee solids which comprises contacting the solution with activated carbon and separating the activated carbon, with caffeine adsorbed thereon, from aqueous solution of reduced caffeine content, characterised in that the activated carbon used is a neutralised carbon that when it is immersed in destilled water the pH value of the water is substantially unchanged.

2. A process according to claim 1 in which the contacting is effected at a temperature of 60°C to 90°C.

3. A process according to claim 1 or claim 2 in which the caffeine content of the aqueous solution is reduced substantially to zero and the non-caffeine green coffee solids therein are combined with green coffee beans having a reduced content of caffeine and of non-caffeine green coffee solids.

4. A process for the removal of caffeine from green coffee beans which comprises contacting the beans with an aqueous medium selected from the group consisting of water, an aqueous solution of non-caffeine green coffee solids and an aqueous solution of non-caffeine green coffee solids containing a minor amount of caffeine, recovering aqueous medium containing caffeine dissolved from the green coffee beans, removing caffeine from the medium, recovering aqueous medium of reduced caffeine content and combining non-caffeine green coffee solids in the aqueous medium of reduced caffeine content with green coffee beans having a reduced content of caffeine and of non-caffeine green coffee solids, characterised in that the caffeine is removed by the process for recovering caffeine claimed in claim 1 or claim 2.

5. A process according to claim 4 in which the caffeine content of the aqueous medium is reduced substantially to zero.

6. A process according to claim 4 or claim 5 in which the ratio of aqueous medium to green coffee beans is 3: 1 to 15 : 1.

7. A process according to any one of claims 1 to 6 in which the aqueous solution or medium containing caffeine contacted with activated carbon has a solids content not exceeding 10 % by weight.

Patentansprüche

1. Verfahren zum Abtrennen van Koffein aus einer wäßrigen Lösung, die aus gen Kaffeebohnen extrahiertes Koffein und koffeinfreie Feststoffe von grünem Kaffee enthält, bei welchem die Lösung mit Aktivkohle in Berührung gebracht wird und die Aktivkohle mit dem daran adsorbierten Koffein aus der wäßrigen Lösung mit verringertem Koffeingehalt abgetrennt wird, dadurch gekennzeichnet, daß die verwendete Aktivkohle eine neutralisierte Kohle ist, so daß, wenn sie in destilliertes Wasser eingetaucht wird, der pH-Wert des Wassers weitgehend unverändert bleibt.

2. Verfahren nach Anspruch 1, bei welchem das Inberührungbringen bei einer Temperatur von 60 bis 90° C durchgeführt wird.

3. Verfahren nach Anspruch 1 oder 2, bei welchem der Koffeingehalt der wäßrigen Lösung auf praktisch Null verringert und die darin enthaltenen koffeinfreien Feststoffe von grünem Kaffee mit grünen Kaffeebohnen, die einen verringerten Gehalt an Koffein und koffeinfreien Feststoffen von grünem Kaffee aufweisen, vereinigt werden.

4. Verfahren zum Abtrennen von Koffein aus grünen Kaffeebohnen, bei welchem die Bohnen mit einem wäßrigen Medium, das aus Wasser, einer wäßrigen Lösung von koffeinfreien Feststoffen von grünem Kaffee und einer wäßrigen Lösung von koffeinfreien Feststoffen von grünem Kaffee mit einem kleineren Gehalt an Koffein ausgewählt ist, in Berührung gebracht werden, wäßriges Medium, das aus den grünen Kaffeebohnen

herausgelöstes Koffein enthält, abgetrennt wird, Koffein aus dem Medium entfernt wird, wäßriges Medium mit verringertem Koffeingehalt abgetrennt wird und koffeinfreie Feststoffe von grünem Kaffee, die im wäßrigen Medium mit verringertem Koffeingehalt anwesend sind, mit grünen Kaffeebohnen, die einen verringerten Gehalt an Koffein und koffeinfreien Feststoffen von grünem Kaffee aufweisen, vereinigt werden, dadurch gekennzeichnet, daß das Koffein durch das in Anspruch 1 oder Anspruch 2 beanspruchte Verfahren zum Abtrennen von Koffein entfernt wird.

5. Verfahren nach Anspruch 4, bei welchem der Koffeingehalt des wäßrigen Mediums auf im wesentlichen Null verringert wird.

6. Verfahren nach Anspruch 4 oder 5, bei welchem das Verhältnis des wäßrigen Mediums zu den grünen Kaffeebohnen 3 : 1 bis 15 : 1 beträgt.

7. Verfahren nach einem der Ansprüche 1 bis 6, bei welchem die wäßrige Lösung oder das wäßrige Medium, die bzw. das Koffein enthält und mit Aktivkohle in Berührung gebracht wird, einen Feststoffgehalt nicht über 10 Gew.-% aufweist.

Revendications

1. Procédé pour la récupération de caféine à partir d'une solution aqueuse de caféine extraite de grains de café vert et de matières solides de café vert sans caféine, qui consiste à mettre en contact la solution avec du charbon activé et à séparer le charbon activé, sur lequel la caféine est adsorbée, de la solution aqueuse à teneur en caféine réduite, caractérisé en ce que le charbon activé utilisé est un charbon neutralisé tel que, lorsqu'il est immergé dans de l'eau distillée, la valeur du pH de l'eau est sensiblement inchangée.

2. Procédé selon la revendication 1, dans lequel le contact est effectué à une température de 60° C à 90° C.

3. Procédé selon la revendication 1 ou la revendication 2, dans lequel la teneur en caféine de la solution aqueuse est réduite sensiblement à zéro et les matières solides de café vert sans caféine qu'elle contient sont combinées à des grains de café vert ayant une teneur réduite en caféine et en matières solides de café vert sans caféine.

4. Procédé pour éliminer la caféine de grains de café vert, qui consiste à mettre en contact les grains avec un milieu aqueux choisi dans les groupes constitués de l'eau, d'une solution aqueuse de matières solides de café vert sans caféine et d'une solution aqueuse de matières solides de café vert sans caféine contenant une petite quantité de caféine, à récupérer un milieu aqueux contenant de la caféine dissoute à partir des grains de café vert, à éliminer la caféine du milieu, à récupérer un milieu aqueux à teneur en caféine réduite et à combiner les matières solides de café vert sans caféine dans le milieu aqueux à teneur en caféine réduite, avec des grains de café vert ayant une teneur réduite en caféine et en matières solides de café vert sans caféine, caractérisé en ce que la caféine est retirée par le procédé de récupération de la caféine selon la revendication 1 ou la revendication 2.

5. Procédé selon la revendication 4, dans lequel la teneur en caféine du milieu aqueux est réduite sensiblement à zéro.

6. Procédé selon la revendication 4 ou la revendication 5, dans lequel le rapport du milieu aqueux aux grains de café vert est de 3 : 1 à 15 : 1.

7. Procédé selon l'une quelconque des revendications 1 à 6, dans lequel la solution ou le milieu aqueux contenant de la caféine, mis en contact avec du charbon activé, possède une teneur en solides ne dépassant pas 10 % en poids.